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(54) IMPROVEMENTS IN OR RELATING TO SWEETENING COMPOSITIONS

(71) We, ORSYMONDE, of 17 rue du Faubourg Montmartre, Paris 9, France, a French Body Corporate, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention concerns new sweetening or sugar-like compositions which are substantially non-calorie-containing, comprising essentially certain synthetic sweetening substances or synthetic sweeteners in combination and also carriers. The invention also concerns methods of making these compositions and their manufacture in the form of pieces of regular shapes.

By the expression "sweetening substance or synthetic sweetener" is meant certain compounds which are not found in nature and are prepared synthetically. Such substances have a sugar-like taste more intense than that of saccharose, without having the corresponding nutritive value. They are useful in the dietic treatment of patients who have to avoid taking sugar, especially beverages containing sugar.

The disorders which come into question in this respect include certain forms of diarrhoea, alimentary obesity and diabetes.

The use of a simple tablet is disagreeable to some of these patients. Attempts have already been made to impart to artificial sweeteners an appearance which resembles that of pieces of natural sugar.

It is for this purpose, especially, that portions of sugar, associated with saccharine, have been prepared in agglomerated or blown (souffléd) form, using a method of manufacture similar to that used for obtaining "puffed wheat" from cereal grains. The disadvantage of these products is that they still contain saccharose.

Accordingly the present invention seeks to provide new sweetening substances or synthetic sweeteners which minimise the disadvantages of the known compositions.

According to one aspect of the invention, a process of preparation of compositions containing sweetening substances or synthetic sweeteners in a regular geometric form having the appearance of lump sugar is provided, which comprises forming the starting ingredients constituted by sweetening substances or synthetic sweeteners and excipients into an aqueous solution, lyophilising the aqueous solution obtained and transforming the lyophilised product into lumps of regular form selected from parallelipipeds, cubes, truncated pyramids and similar shapes.

The present invention relates more particularly to the preparation of sweetening compositions or synthetic sweeteners, based upon saccharinates of metals such as sodium, in the form of products having the appearance of lump sugar. This form particularly offers facility of use and a psychological advantage for patients treated with non-calorie-containing, i.e. non-fattening, sweetening agents; also, the compositions of the invention have the property of substantially dissolution in water and in drinks, because of their porous nature.

According to another aspect, the invention also concerns novel forms of lumps of the sweetening compositions for presentation to the public, namely individual trays each containing a predetermined number of lumps of the composition. By way of example, each tray contains 25 to 50 portions of the sweetening composition.

According to another feature, the present invention concerns the process of preparation of the composition directly in compartments or containers for commercial and other presentation.

The novel sweetening compositions of the present invention comprise a sweetening agent

in the form of a derivative of saccharine, preferably sodium saccharinate. The compositions can also contain, in particular, phloroglucinol. Additives and excipients which can also be included in the compositions particularly include gum arabic and, in general, hydrophilic and adhesive substances which allow the characteristic of instantaneous dissolution of the final products to be improved. Reference can be made among substances of this class to non-ionic surface-active agents, such as the polyoxyethylene-polyoxypropanediol-1,2 products commercially available under the trade name "Pluronic" and manufactured by Wyandotte, particularly Pluronic F 68 also known under the name RC 102, and polyvinyl-alcohol, particularly the product commercially available under the name Rhodiovol 25/100 and marketed by Rhone-Poulenc. The compositions of the invention also include correcting agents for the taste of saccharine chosen particularly from sodium, calcium and magnesium cyclamates, glycolline, vanillin and analogous compounds.

There can also be added to such compositions traces of correctives of the rather bitter taste of saccharine in the form of saline substances, for instance sodium chloride. Glycocol is preferably used in quantities at the most equal to 60% by weight of the total sweetening mass. Vanillin is preferably present at a minimum in the ratio of 0.5% and preferably 1% by weight of the total sweetening mass. At vanillin concentrations lower than those mentioned, the after-taste of saccharine is not masked, while at higher concentrations the taste of vanillin is too marked.

As regards phloroglucinol, sodium saccharinate and cyclamates in particular, it may be mentioned that these are substances known for their sweetening property and their very low toxicity. Their use is thus preferred in the scope of the present invention.

According to a preferred feature of the invention, the process of preparation of the composition in the form of lumps comprises subjecting aqueous solutions of the ingredients selected to form the composition to lyophilisation in trays each having a series of forming receptacles, that is individual compartments having suitable dimensions for serving as receptacles for lumps of the final product. This process allows a cellular product of lump form to be made in a single operation. The compositions obtained preserve the volume of the initial solution defined by each individual compartment, while air has replaced the water of the solution, at the end of the process, thus giving the product its porosity.

The fundamental method of formation of the compositions of the invention is as follows:

An aqueous solution is prepared corresponding to the following formula, in such a manner that the volume of the final product contains a unit dose of the active ingredients; to this solution is added different types and quantities of carrier, so that each solution obtained corresponds to the general formula desired.

The process of the invention is then carried out, by freezing the aqueous initial solution in trays at a low temperature, that is at −18° to −40°C., then subjecting them to cryodessication or lyophilisation at a low pressure of about 10^{-2} mm Hg, such that the necessary heat to sublime the water is provided at a temperature which does not rise above the freezing point of the product.

According to another form of the method of the invention, the partition members of the preparation trays forming the individual compartments are siliconised, which avoids adhesion of the lumps or blocks of the final product to the walls of the partitions and facilitates their extraction at the end of the process. It has surprisingly been found that the best results are thereby obtained, from the standpoint of facility of extraction of the final lumps or pieces of the sweetening product and thus from the standpoint of maintenance of such product in the desired regular form.

It has been found particularly advantageous for this purpose to use the silicone available commercially from Rhone-Poulenc under the name Rhodorsil resin 4673 or Rhodorsil EIP 35%. This silicone has the following properties:

Its dry extract is 73%; it is soluble in white spirit-butanol. It can be diluted with the following thinners: ethyl acetate, aromatic, aliphatic and chlorinated hydrocarbons. Its specific gravity at 20°C. is about 1.00. Its viscosity (in cSt) at 20°C. is 7/15. Its flash point is 34°. Drying conditions render it tackfree after about 4 hours. Its curing conditions are 24 hrs. at 20°C. or 30 minutes at 140°C.

The present invention also allows the physical characteristics, particularly the consistency and structure of the sweetening compositions, to be improved.

Also, by suitable selection of the carriers mentioned, a desired consistency can be imparted to the mass, which is useful during its final conditioning.

Furthermore, the freezing of the solutions can be done under conditions suitable for modifying the structure and increasing the fineness of the crystals. For example, the freezing can be carried out on vibrating plates, driven by electromagnetic or ultrasonic vibrations.

The material preferred for manufacture of the trays is PVC (non-plasticised polyvinyl chloride, alimentary quality, thickness 500 microns).

This material was chosen for its rigidity, good impermeability to gas and water vapour, and adequate thermal conductivity. It has been tested and showed no deterioration of appearance or impermeability on the rapid freezing inherent in the technique of lyophilisation. It was also observed that the portions of the composition of the invention do not adhere to the walls of PVC after lyophilisation. It is also possible to use low pressure polyethylene for the trays, as it is not affected by intense cooling, forms a usefully tight seal and does not stick to the composition of the invention, though it does not have the rigidity of PVC.

The partitions can be made of PVC, for example, opaque PVC, or metal, for example stainless steel, silvered brass or other suitable material. As indicated above, a siliconised partition is preferably used.

For presentation, i.e. get-up, of the sweetening composition of the invention its form of use, two groups of presentations have been developed:

The first group rests upon the fact that the operation of lyophilisation is carried out in the compartments which serve as receptacles for the portions of the composition of the invention, in presentation to the public.

For presentations of the second group, lyophilisation is carried out in the standard way and yields slabs of large dimensions, which can be cut up on leaving the lyophilisation apparatus and divided into small pieces. Conditioning of the trays can be carried out as follows:

The trays leaving the lyophilising apparatus are received in an air-conditioned chamber and stacked in this chamber, with 30-thousandth gauge aluminium foil coated with PVC.

The stacked trays are then placed in a flexible cover.

According to another procedure, utilizing siliconised partitions in the method, the operations of conditioning were as follows:

The vessels were removed from the lyophilisation apparatus. A pad of cellulose, a leaflet and a small plastic holder, to allow the user to "select" each small lump, were placed over the cubes or portions of the final composition. A cover was placed around each container. The box was closed by a strip of adhesive material, for example "Scotch" tape. Finally, the box was placed in a cardboard carton to which was joined a smaller "free sample" carton of plastics material containing several extra lumps, for instance, 5 lumps for a main box of 50 lumps.

By way of example, a presentation tray has the following dimensions: depth about 10 mm, width about 50 mm and length about 125 mm.

Dividers are located inside the tray, for example 4 longitudinal dividers and 4 transverse dividers, forming 25 compartments of rectangular parallelepiped form, for receiving lumps of the sweetening composition of the invention.

In this case, the lumps obtained have the form of rectangular parallelepipeds measuring approximately $25 \times 10 \times 8$ mm. Their volume is about 2 ml.

Naturally, the dimensions of the trays and of the compartments can be varied according to the products desired.

The shape of the compartments can also be varied and so impart to the lumps of the product any regular shape desired.

For example, presentation can take the form of 50 lumps each of about 1 cc.

In certain cases, it is preferable to present the non-fattening sweetener in the form of larger lumps which thus resemble certain varieties of commercial lump sugar. This result is obtained by previously diluting the starting materials, i.e. by using a larger amount of water. Thus lumps of about 1.6 cc in size can be obtained, by diluting, from the same quantities of starting materials as those used to make small lumps about 1 cc in size.

The product obtained, from a lyophilisation can be got up for presentation from the initial blocks, for example, according to any one of the four ways A to D below:

A. The PVC trays included partitions with 25 to 50 compartments, also of PVC and integral with the tray.

The commercial model thus contained 25 to 50 parallelepipeds of the composition of the invention, each located in a small compartment of PVC.

B. The lyophilisation was performed in PVC trays in which was inserted, after filling with the necessary quantity of liquid, a stationary partition of stainless steel.

When the lyophilisation is finished, the partition is removed, in an air-conditioned chamber, and is detached very easily, stacking can be effected as mentioned above.

The commercial model gives 25 to 50 parallelepipeds of the composition of the invention which are loosely packed in the tray.

C. The lyophilisation is performed in PVC trays without partitions.

On leaving the lyophilising apparatus, always in an air-conditioned chamber, the block is divided, in the tray used for lyophilisation, by a guillotine into 25 to 50 portions of equal volume.

D. The lyophilisation is performed in PVC trays having ribs on the inside dividing the base into 25 to 50 equal rectangles. The trays can be stacked as mentioned before. When the aluminium foil separators have been removed, the tray is inverted and a single block is obtained divided by grooves into 25 to 50 rectangles which are easily broken into individual portions.

According to an embodiment of the second group of presentations obtained by the classical method of lyophilising apparatus are stacked in an air-conditioned chamber and cut by a guillotine into rectangular parallelepipeds of 1 or 2 cubic centimetres.

The parallelepipeds are individually wrapped in aluminium foil and conditioned in groups of 25 to 50 in a box.

The following examples illustrate compositions of the present invention without limiting the extent or scope of the invention.

Examples 1, 2, 8 to 10 relate to the process of the invention using siliconised partitions.

Examples 3 to 7 illustrate the invention without siliconisation of the partitions.

EXAMPLE 1

Tests have been carried out for effecting the process of the invention in the laboratory with a commercial lyophilisation apparatus known under the name of Sogev-Serail RP 2. The trays used were made of polyvinyl chloride (PVC). A partition of metallic material, such as silvered brass, forming a "lining" was formed, in order to facilitate extraction of the blocks of the final product, and was siliconised with Rhodorsil EIP 35%. For this purpose, the walls of the metallic partition assembly were coated with the silicone by successively effecting dissolution of the compound in water demineralised to 10%, submersion of the assembly in the solution for 2 minutes, draining, wrapping in aluminium foil and polymerisation for one hour at 180°C.

The operation of lyophilisation was carried out with aqueous solutions containing the sweetening agents and excipients mentioned.

The tray and partition assembly were cooled in the container of the lyophilisation apparatus. A temperature of about −45°C. was reached in 15 minutes. The vessel was filled with 50 ml of solution to be treated and the partition assembly was put into place.

The entire assembly was located in a cooled enclosure. The mass attained a temperature of −35°C. in about ½ hour. It appeared advantageous for solidification to take place as rapidly as possible. Cooling was then arrested and the assembly was allowed to undergo normal heating. The temperature of the mass remained at −25°C. for several hours. During this time, the ambient temperature passed from −40°C. to +5° to +10°C.

The vacuum utilised during the operation was about 10^{-2} mm Hg. The operation of lyophilisation was continued for 12 hours. The next day, the temperature of the material had become the ambient temperature of about 20°C. The lyophilisation was ended.

The product obtained by lyophilisation was not particularly hygroscopic. It was thus not necessary to effect removal of the trays from the lyophilisation apparatus in a very dry atmosphere. An atmosphere of a moisture content of the order of 50° was suitable.

Conditioning of the lumps of final product was then effected by the methods mentioned above.

EXAMPLE 2

This example is more particularly directed to an industrial method of presentation of the products of the invention.

In this case, the product was produced in a container of PVC (thickness 500 microns), which was opaque and had a volume of about 55 ml. The PVC material selected was a non-plasticised polyvinyl chloride of alimentary quality. This vessel included a partition member which was also formed of opaque PVC, which separated 50 small blocks each having the form of a truncated pyramid and a volume of approximately 1 cc. The tray was covered with a lid of opaque or transparent PVC.

EXAMPLE 3

A composition of the following formula was prepared, in order to carry out the process of the invention:

	For 100 g. solution, before lyophilisation	Per 2 ml portion, after lyophilisation
Sodium cyclamate	12.500 g.	0.250 g.
Sodium saccharinate	1.250 g.	0.025 g.
Phloroglucinol	0.005 g.	0.0001 g.
Gum arabic	10.000 g.	0.20 g.
Pluronic F 68 (manufactured by the Wyandotte Company)	2.500 g.	0.05 g.
Water, to make 100 ml.		0.5251 g.

EXAMPLE 4

The same formation was made up as in Example 1, but the phloroglucinol was replaced by 0.01 g. of sodium chloride per 2 ml of final product after lyophilisation.

EXAMPLE 5

Phloroglucinol	0.01 g.
Sodium saccharinate	1 g.
Sodium cyclamate	12.5 g.
Gum arabic	5 g.
Rhodoviol 25/100 (polyvinyl alcohol, available commercially from Societe Rhone Poulenc)	1 g.
Water	to make 100 ml.

EXAMPLE 6

The process of the invention was carried out with following formulation:

Phloroglucinol	0.005 g.
Sodium saccharinate	1.25 g.
Calcium cyclamate	12.5 g.
Gum arabic	5 g.
Rhodoviol 25/100	1 g.
Water	to make 100 ml.

EXAMPLE 7

The process of the invention was carried out with the following formulation:

Phloroglucinol	0.005 g.
Sodium saccharinate	1.25 g.
Sodium cyclamate	12.5 g.
Gum arabic	8 g.
Glycocol	5 g.
Water	to make 100 ml.

In the foregoing Examples 3 to 7, the quantity of sweetener has been calculated so that a piece of the composition of the invention has approximately the sweetening power of two ordinary lumps of sugar (or 2 to 5 g.). This is that a sweetening power of about 250 g. of sugar corresponds to a tray of 25 pieces of the composition of the invention, each piece having a volume of about 2 ml as indicated in the above text.

EXAMPLE 8

Preparation of a cyclamate-free sweetening composition in small lumps.

An aqueous solution containing the following ingredients per 50 ml of solution was prepared:

Ingredients	Weight in g.
Sodium saccharinate	1.25
RC-102	0.7485
Glycocol	8.0
Gum arabic	5.0
Vanillin	0.0015
Water q.s.	50 ml.

The solution so obtained was subjected to the method of Example 1 and cubes of a sweetening composition were obtained having the following composition for a volume of 1 cc per cube:

Ingredients	Weight in g.
Sodium saccharinate	0.025
RC-102	0.01497
Glycocol	0.16
Gum arabic	0.10
Vanillin	0.00003
Total weight of cube	0.30000 g.

Each cube has a sweetening power which is equivalent to about that of 7.50 g. of sugar (1 large or no. 3 portion of commerce, or 1½ small or no. 4 portions of commerce).

The cubes prepared according to the present Example are considered to be "small" lumps.

Approximate dimensions:

Overall surface	— 12 mm × 10 mm
Thickness	— 10 mm
Volume	— 1.0 cm^3
Weight	— 0.30 g.

EXAMPLE 9

Preparation of a cyclamate-free sweetening composition in large portions.

An aqueous solution was prepared with the ingredients of Example 8 using a greater dilution by water.

By using the method of Example 1, cubes of the sweetening composition were obtained having the following composition for a volume of about 1.6 cc per cube:

Ingredients	Weight in g.
Sodium saccharinate	0.025
RC-102	0.023
Glycocol	0.265
Gum arabic	0.157
Vanillin	0.000047
Total weight of cube	0.470047 g.

The cubes prepared according to the present Example are considered to be "large" lumps.

Approximate dimensions:

Overall surface	— 15 mm × 13 mm
Thickness	— 10 mm
Volume	— 1.6 cm^3
Weight	— 0.47 g.

EXAMPLE 10

Preparation of a sweetening composition containing phloroglucinol, but free from cyclamates

Preparation was carried out as in the preceding Examples, using an aqueous solution containing the following ingredients:

Ingredients	Weight in mg.
Phloroglucinol	0.0025
Sodium saccharinate	1.25
RC-102	0.7485
Glycocol	8
Gum arabic	5
Vanillin	0.0015
Water q.s.	50 ml.

Sweetening compositions were finally obtained as follows:

Ingredients	Weight in g. for a cube of 0.3 g. in volume (small lump)	Weight in g. for a cube of 0.47 g. in volume (large lump)
Phloroglucinol	0.0005	0.00065
Sodium saccharinate	0.025	0.025
RC-102	0.015	0.023
Glycocol	0.16	0.265
Gum arabic	0.10	0.157
Vanillin	0.00003	0.000047

The compositions prepared according to the foregoing Examples have been tested particularly by tasting and the results obtained show that they constitute non-fattening sweetening agents which are very satisfactory for the patients treated. In particular, the sweetening power of the compositions of the invention is excellent. They have been used for a period of 6 months by diabetics without any sign of intolerance.

EXAMPLE 11

Preparation of a sweetening composition in portions of high hardness which are only slightly friable, not starting from a very diluted solution but from a solution having a less fluid consistency.

The procedure uses the following ingredients:

Sodium saccharinate	2 g.
Powdered Gum arabic	3 g.
Fine crystals of Glycocol	55 g.
Water	15 g.

The saccharinate was finely pulverised and then mixed with the gum arabic, also in the form of a fine powder. The glycocol was then added in accordance with its nature (in fine crystals to avoid lumps), when the mixture of the powders was finished, and then the water was incorporated. A pasty liquid was obtained which was introduced into trays for lyophilisation. This was carried out in a refrigerator at —18°C.

The quantity indicated above allowed a tray of plastics material of 50 ccs to be filled.

The sequence of operations was carried out as indicated in the foregoing Examples.

EXAMPLE 12

Preparation of a sweetening agent in slightly friable lumps.

The following ingredients were utilised:

Sodium saccharinate	0.025 g.
RC-102	0.023 g.
Glycocol	0.6875 g.
Gum arabic	0.0375 g.
Vanillin	0.00004 g.

The water to be incorporated in order to obtain a pasty liquid as in Example 11 was 0.1875 g. (that is to say about 24% by weight of the dry mass). The 95% ethyl alcohol necessary for dissolving the vanillin was 0.004 g. The alcoholic vanillin solution was incorporated in the mass like the water.

The quantities of glycol, gum arabic and water can be varied in the following percentage proportions of the dry mass in the formula containing 4.20 g % of sodium saccharinate:

Glycocol	— 70	to 95 g %	weight of the dry mass
Gum arabic	— 0.5	to 15 g %	„ „ „ „ „
Water	— 3	to 75 g %	„ „ „ „ „

Lyophilisation was carried out as in Example 11.

The formulae of the lumps of the sweetening composition corresponding to the foregoing Examples can also serve as excipients for, on the one hand, medicaments such as acetyl-salicylic acid, corticoids, agents for modifying fertility, theobromine, beer yeast or other slightly soluble medicaments and, on the other hand, medicaments which are soluble but which certain patients prefer in solution more than as tablets or capsules such as nicethamide, caffeine, sodium bromide, sodium methylarsinate and others. In the latter case, the lumps of the composition containing the medicaments, because of their instantaneous dissolution in water, serve to reconstitute the solutions desired. The compositions of the invention thus form solid carriers having a sweetening nature, allowing masking of the taste produced by various products which are intended for oral administration. Moreover, the presentation of these products, such as medicaments, in lumps of regular shape including the compositions of the invention offers advantages which have not been known previously.

We are aware of The Artificial Sweeteners in Food Regulations, 1969, and we make no claim to use the invention in contravention of the law.

WHAT WE CLAIM IS:—

1. A process of preparation of compositions containing sweetening substances or synthetic sweeteners in a regular geometric form having the appearance of lump sugar, which comprises forming the starting ingredients constituted by sweetening substances or synthetic sweeteners and excipients into an aqueous solution, lyophilising the aqueous solution obtained and transforming the lyophilised product into lumps of regular form selected from parallelepipeds, cubes, truncated pyramids and similar shapes.

2. A process according to claim 1, in which transformation of the lyophilised product into lumps is effected by cutting.

3. A process according to claim 1, in which the lyophilisation is effected in trays serving for containing the lumps for commercial presentation.

4. A process according to claim 3, in which lyophilistaion is carried out in trays having ribs on their interior bases, the lyophilised product having a final shape allowing it to be broken into individual lumps, the ribs thus forming a rectangular system of grooves in the product along which fracture may occur easily.

5. A process according to claim 3, in which transformation of the composition into lumps is effected during lyophilisation in trays provided with partitions defining compartments for the lumps.

6. A process according to claim 5, in which the partitions are integral with the trays.

7. A process according to claim 5, in which the compartments are movable.

8. A process according to claim 5, 6 or 7, in which the trays and the partitions are formed of plastics material.

9. A process according to claim 5, 6 or 7, in which the partitions are made of metals or alloys.

10. A process according to claim 8, in which the plastics material is selected from polyvinyl chloride, and low pressure polyethylene.

11. A process according to claim 9, in which the metals and alloys are selected from stainless steel and silvered brass.

12. A process according to any of claims 5 to 11, in which the partitions are provided with a silicone coating.

13. A process according to claim 12, in which the silicone is the product known commercially under the name Rhodorsil resin 4673.

14. Sweetening compositions in the form of lumps characterised by instantaneous dissolution in water, when prepared by a process according to any of the foregoing claims.

15. Sweetening compositions according to claim 14, in lyophilisation trays without partitions.

16. Sweetening compositions according to claim 14, in lyophilisation trays and located in receptacles defined by partitions.

17. Sweetening compositions in lumps according to claims 14 to 16, characterised by a very hard and slightly friable texture.

18. Sweetening excipients in lumps capable of instantaneous dissolution in water and beverages for medicaments and foodstuffs, characterised in that they include compositions according to claims 14 to 17.

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